Mathematical Modeling of Aerosol Formation from Binary Vapor Mixtures

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Abstract

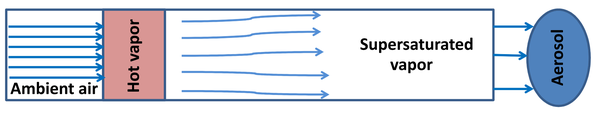
Electronic Nicotine Delivery Systems (ENDSs) produce condensation aerosol by mixing a high temperature vapor mixture with ambient air, resulting in a vapor mixture at high supersaturation. Nucleation theories and thermodynamics can be used to characterize droplet size distribution, droplet composition as well as vapor-liquid partitioning. In circumstances where the supersaturation is very high, and the critical cluster size is smaller than a dimer, the Classical Nucleation Theory (CNT) does not apply.

We addressed this limitation by developing a computational model that uses kinetic theory of gases to calculate nucleation rate and aerosol formation for binary mixtures of propylene glycol (PG) and glycerol (G) vapors. The process involves ternary collisions of two vapor molecules of different kinds and any third molecule. The model accounts for (i) non-isothermal growth of clusters with free molecular regime approximation where the cluster size is much smaller than the mean free path of vapor molecules, (ii) the latent heat of phase change, that affects the temperature difference between clusters of molecules and gaseous mixture. An ideal liquid mixture solution was assumed for the droplets to account for the vapor-liquid partitioning of each constituent. Coagulation is the primary mechanism of droplet growth after 200 ns of free molecular condensation.

Computations were performed for different PG/G mixture ratios, ranging from 0/100 to 100/0 (mole based). Under ideal adiabatic mixing with air, at a vapor temperature of 570 K (close to glycerol boiling temperature), the initial supersaturation of glycerin drops several orders of magnitude. Particle size distribution over time and particle composition were calculated. It was shown that final droplet size distribution is determined by coagulation. The temperatures of droplets and gaseous mixture are the same, due to a high heat transfer coefficient at the particle-gas interface. The droplet composition for PG/G mixture strongly depends on the glycerol partial supersaturation in the initial mixture. The mass median diameter of aerosol particles, 1 s after mixing reaches 1-1.5 μm, and shows small dependence on the PG/G ratio and temperature. For all practical purpose, coagulation stops when the number density of micron-size droplets decreases to less than about 10^{14} droplets/m^3.

Model Development

Electronic Nicotine Delivery System (ENDS): Aerosol formation



- An e-liquid containing **propylene glycol (PG)** and **glycerol (G)** and **nicotine** evaporates.
- The air cools the hot vapor.
- Aerosol particles form from supersaturated vapor.

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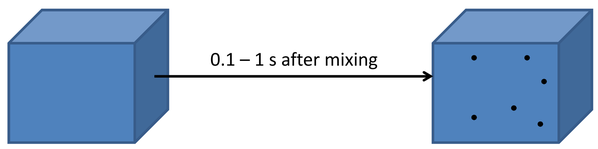
A problem to model



KNOWNS:
- Small homogeneous volume
- Its initial composition
- Its initial temperature

UNKNOWNS:
- Vapor composition and temperature
- Droplets composition and temperature
- Aerosol size distribution

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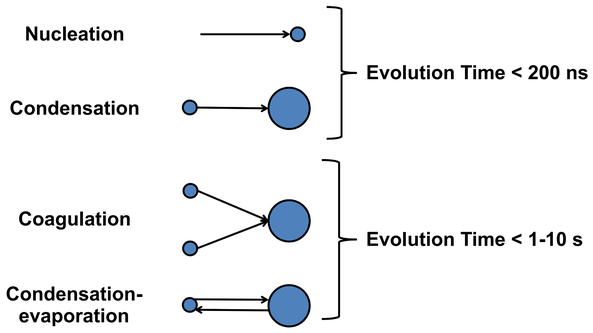
Physical phenomena to consider



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Initial conditions for mixtures of PG and G

Supersaturation: $S = \dfrac{\text{Vapor Partial Pressure}}{\text{Saturation Vapor Pressure}}$

PG/G (mole fractions)	0.1/0.9	0.3/0.7	0.5/0.5	0.7/0.3	0.9/0.1
S_{PG}	0.9	2.6	4.24	5.76	7.9
S_G	1759	1313	900	518.6	166
$T_{mixture}$	338	338.5	338.9	339.4	339.8

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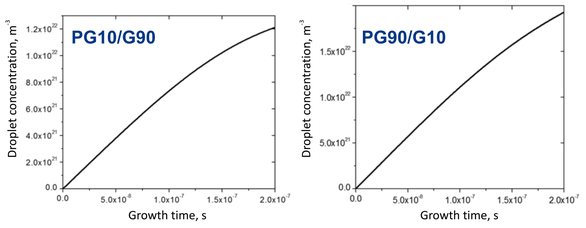
Nucleation rates

- Classical nucleation theory does not apply at high supersaturations.
- Rate of ternary collisions between air and vapor molecules controls the nucleation rate.

$$\frac{d(\text{Droplet Concentration})}{dt} = \text{Rate of ternary collisions}$$



$$\frac{dn_d}{dt} = \sum_{i \le j} I_{ij}$$

$$I_{ij} = n_i n_j \sqrt{\frac{8kT}{\pi m_i}} \frac{4\pi^2}{3} R_{ij}^5 \frac{P}{kT_g} \qquad R_{ij} = \left(\frac{3}{4\pi}\right)^{\frac{1}{3}} (V_{li} V_{lj})^{1/6}$$

n_d	**Concentration of liquid clusters,**	**m^{-3}**
n_i	**Concentration of i in gas,**	**m^{-3}**
m_i	**Mass of a molecule i,**	**kg**
V_{li}	**Molecular volume of i in liquid phase,**	**m^3**
T_d	**Temperature of liquid cluster,**	**K**
T_g	**Temperature of the gas,**	**K**

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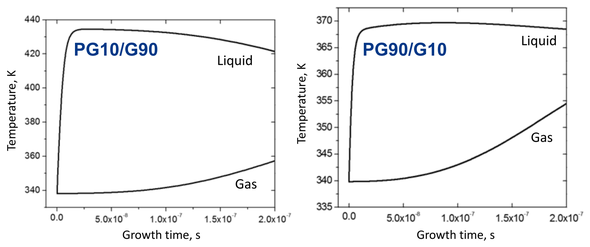
Temperature from energy balance

- Release of latent heat of condensation heats up the system.
- Molecular collisions cause heat transfer between droplets and vapor.

$$\frac{d(c_{gas}T_{gas})}{dt} = \text{Energy Flux} \times \text{Droplet Surface Area}$$

$$\frac{d(c_{liquid}T_{liquid})}{dt} = -\text{Energy Flux} \times \text{Droplet Surface Area}$$



$$\frac{dT_d}{dt} + T_d \frac{\sum_i m_i \frac{dV_i}{dt}}{\sum_i m_i V_i} = \frac{3q}{c_l \rho_l R_d}; \qquad T_g \frac{\sum_i c_i \frac{dn_i}{dt}}{c_a n_a + \sum_i c_i n_i} + \frac{dT_g}{dt} = -\frac{4\pi R_d^2 n_d q}{c_a n_a + \sum_i c_i n_i}$$

$$q = \sum_i \sqrt{\frac{kT_g}{2\pi m_i}} n_i(T_g)\left(c_i T_g + h_i + \frac{1}{2}kT_g\right) + \sqrt{\frac{kT_g}{2\pi m_a}} n_a(T_g)\left(c_a T_g + \frac{1}{2}k(T_g)\right) - \left[\sum_i \sqrt{\frac{kT_d}{2\pi m_i}} x_i n_{si}(T_d)\left(c_i T_d + h_i + \frac{1}{2}kT_d\right) + \sqrt{\frac{kT_d}{2\pi m_a}} n_a(T_d)\left(c_a T_d + \frac{1}{2}k(T_d)\right)\right]$$

c_i	**Heat capacities per molecule at constant temperature and pressure,**	**J/K**
ν_i	**Number of i molecules in a liquid cluster,**	**dimensionless**
ρ_l	**Mass density of liquid,**	**kg/m³**
c_l	**Specific heat for liquid mixture,**	**J/kg-K**
R_d	**Radius of a liquid cluster,**	**m**
q	**Heat flux,**	**J $m^{-2}s^{-1}$**
n_i	**Concentration of i in gas,**	**m^{-3}**
h_i	**Enthalpy of vaporization of i per molecule,**	**J**
x_i	**Mole fraction of i in liquid,**	**dimensionless**

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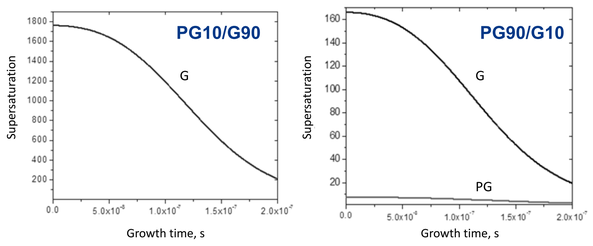
Vapor composition from mass balance

- Condensation significantly depletes PG and G in the vapor during the initial 200 ns.

$$\frac{d(\text{G concentration})}{dt} = \text{Molecular Flux of G} \times \text{Droplet Surface Area}$$

$$\frac{d(\text{PG concentration})}{dt} = \text{Molecular Flux of PG} \times \text{Droplet Surface Area}$$



$$\frac{dV_i}{dt} = 4\pi {R_d}^2 J_i; \qquad \frac{dn_i}{dt} = -4\pi {R_d}^2 n_d J_i$$

$$J_i = \sqrt{\frac{k}{2\pi m_i}}\left[\sqrt{T_g} n_i - \sqrt{T_d} x_i n_{si}(T_d)\right]$$

J_i	**Net condensation flux of i,**	**$m^{-2}s^{-1}$**

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Monodisperse coagulation of droplets

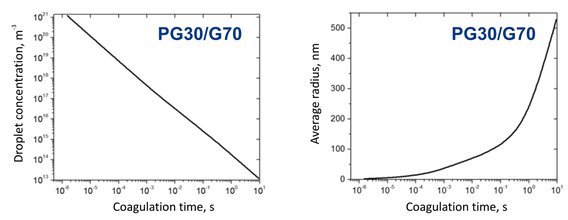
- Monodisperse coagulation in free-molecular regime:

$$\frac{dN(t)}{dt} = -KN^2 \qquad K = 4\pi R^2 \sqrt{2kT/m_d} \sim R^{0.5}$$

- Mass conservation determines sizes of droplets:

$$N_0\langle R_0^3\rangle = N(t)\langle R^3(t)\rangle$$

- Coagulation increases droplet radii by 500 while decreasing their concentration by 10^8.



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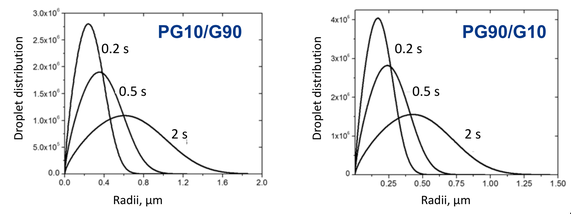
Distribution of droplets in size

- Weibull function $f(r) = \frac{r^{\alpha} e^{-\beta r^3}}{\int_0^{\infty} r^{\alpha} e^{-\beta r^3} dr}$ represents droplet size distribution [1].
- Weibull function maximizes the information entropy.
- Average droplet radii and coalescence determine the parameters α and β.



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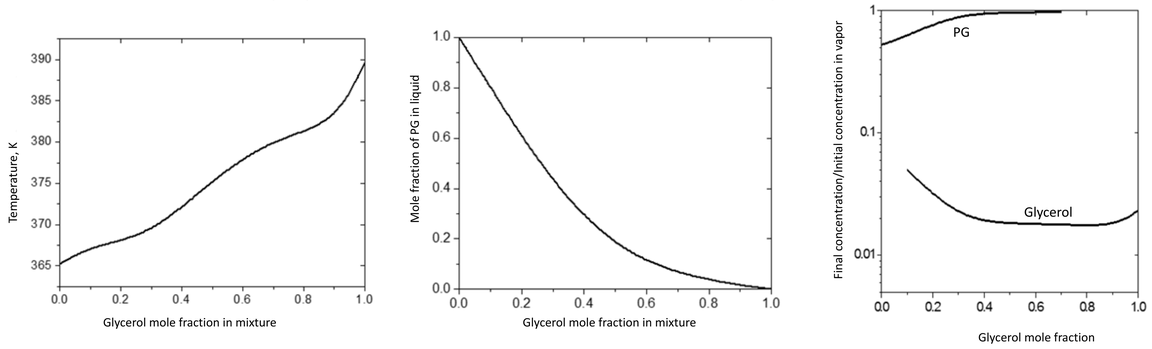
Temperature and composition of various mixtures

- Temperature increases with the G mole fraction due to the higher latent heat for G vs. PG.
- The liquid phase is enriched in G due to the lower saturation vapor pressure for G vs. PG.



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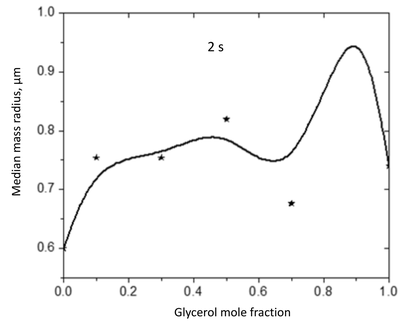
Model Validation

Predictions (—) vs. the experimental data (★) for aerosol median mass radius after 2 s as a function of the composition [2].



Conclusions

- Mixing of vapor and air with a temperature difference over 100 K results in high supersaturations.
- During initial 30-200 ns, nucleation and droplet growth due to condensation dominate the aerosol evolution.
- At later times, Brownian coagulation becomes the principal mechanism of aerosol evolution.
- Comparison with available experimental data suggests that our model is qualitatively consistent with the observed experimental trends.

References

[1] Fisenko SP, et al. Evaporative cooling of water in a mechanical draft cooling tower. International Journal of Heat and Mass Transfer, 2004. 47:165-177.
[2] Baassiri M, et al. Clouds and "throat hit": Effects of liquid composition on nicotine emissions and physical characteristics of electronic cigarette aerosols. Aerosol Science and Technology, 2017. 51:1231-1239.